5

IMPROVED PROCESS FOR THE PRODUCTION AND PURIFICATION OF VI-
NYL AROMATIC MONOMERS

The present invention relates to an improved process
10   for the production and purification of vinyl aromatic mono-
mers.

More specifically, the present invention relates to an
improved process for the production and purification of vi-
nyl aromatic monomers coming from the dehydrogenation of
15   the corresponding alkylated products.

Even more specifically, the present invention relates
to an improved process for the production and purification
of styrene coming from the dehydrogenation of ethyl ben-
zene.

20   Vinyl aromatic monomers, such as styrene, are particu-
larly known for their use in the preparation of plastic ma-
terials, such as compact/crystalline polystyrene or ex-
panded polystyrene. These monomers are recovered from the
liquid effluents coming from a dehydrogenation section by
25   means of a series of fractionation columns operating in se-

ries, with respect to the flow of vinyl aromatic monomer.

In the case of styrene, there are generally three or four fractionation columns depending on the type of process. The liquid mixture of aromatic hydrocarbons coming

5   from the dehydrogenation section is fed into the first column. In this column, a mixture of benzene and toluene is separated at the head, which forms a by-product of the production process of styrene, whereas a stream containing non-reacted ethyl benzene, styrene and high-boiling prod-

10   ucts is extracted from the bottom. The stream coming from the bottom of the first column is fed to a second column, where a stream containing non-reacted ethyl benzene is separated at the head and recycled to the dehydrogenation section, whereas a stream containing styrene together with

15   high-boiling products is extracted from the bottom. The flow coming from the bottom of the second column is fed to a third column, where the styrene forming the end-product is removed at the head, whereas a stream consisting of styrene and high-boiling products is extracted from the bot-

20   tom. As the concentration of styrene present in the stream leaving the bottom of the third purification column is still high, it is further treated in a fourth column, where said stream is fed, or else to a different apparatus, such as an evaporator. A stream rich in high-boiling products

25   which forms the process residue (waste stream) is produced

and removed from the latter part of the purification sec-
tion, whether it be a distillation column or an evaporator.

What is indicated above is one of the possible purifi-
cation schemes of styrene. There is also a second scheme,
5   based on three columns which is described hereafter. In
this case the liquid hydrocarbon mixture is fed to the
first column, where a mixture of benzene, toluene and ethyl
benzene is separated at the top, whereas a stream contain-
ing styrene and high-boiling products is separated at the
10   bottom. The product extracted from the head is fed to a
second column where a mixture of benzene and toluene, which
forms a by-product of the production process of styrene, is
extracted from the head, whereas a stream containing non-
reacted ethyl benzene is obtained at the bottom and is sent
15   to the dehydrogenation unit. The stream coming from the
bottom of the first column is fed to the third column,
where purified styrene is extracted from the head, whereas
a stream whose composition is similar to that described in
the previous scheme, is obtained at the bottom, which, as
20   it is still rich in styrene, is further treated to recover
this with procedures similar to those described above.

The residue (waste stream), produced with both
schemes, contains significant quantities of heavy, viscous
materials consisting of pitches and/or other polymeric
25   products which are formed as a result of the processing

process. Vinyl aromatic monomers, for example styrene, tend to polymerize if they are subjected to the action of heat and consequently, during distillation, they tend to form solid polymeric residues which can be deposited and block

5   the equipment associated with the purification system. In order to avoid or reduce this phenomenon, the purification of styrene requires the use of polymerization retardants or inhibitors such as, for example, stable nitroxide radicals used alone or combined with polymerization retardants such

10   as, for example, aromatic nitro-derivatives, as described in patents US 4,670,131, 5,254,760 and 5,910,232.

The Applicant has now found a new additive for preventing the premature polymerization of vinyl aromatic monomers, coming from the dehydrogenation of the corre-

15   sponding alkylated products, particularly during the purification phase which, in the case of the use of nitroxide alone, strengthens its effect. Alternatively, this additive can substitute the retarding compound, when this is used in a combination with the nitroxide.

20   This new additive comes from the alkylation section which precedes dehydrogenation and consists of heavy products, essentially polyalkyl benzenes, which are formed during the alkylation reaction and which are separated in a specific purification section. It has, in fact, been sur-

25   prisingly found that the heavier stream coming from the

bottom of the distillation section, downstream of the alkylation reactor, if fed to the purification section of the vinyl aromatic monomer, inhibits its premature polymerization. This result is not only unexpected but is also useful

5   as it allows a greater recovery of the monomer from the styrene distillation residues.

An object of the present invention therefore relates to an improved process for the production and purification of vinyl aromatic monomers which comprises:

10   a)   feeding a stream consisting of an aromatic hydrocarbon together with a stream essentially consisting of a C_2-C_3 olefin, to an alkylation section;

     b)   feeding the reaction product coming from the alkylation section to a first separation section;

15   c)   discharging from the first separation section, a first stream consisting of non-reacted aromatic hydrocarbon which is recycled to the alkylation section, a second stream essentially consisting of a mono-alkylated aromatic hydrocarbon, a third stream essentially consist-

20   ing of dialkylated aromatic hydrocarbons, sent to a transalkylation section, and a fourth stream essentially consisting of a mixture of polyalkylated aromatic hydrocarbons;

     d)   feeding the second stream of step (c) to a dehydroge-

25   nation section;

e) feeding the reaction product coming from the dehydro-
    genation section to a second purification/separation
    section, comprising at least one distillation column;

f) feeding the fourth stream of step (c) to said at least

5   one distillation column;

g) discharging from the head of said at least one distil-
    lation column, a stream consisting of the vinyl aro-
    matic monomer having a purity higher than 99.7% by
    weight.

10 According to the present invention, the aromatic hy-
drocarbon fed to the alkylation section can be selected
from those having from 6 to 9 carbon atoms but it prefera-
bly consists of benzene. Another aromatic hydrocarbon which
can be used in the process object of the present invention

15 is, for example, toluene.

The preferred aromatic hydrocarbon is benzene refinery
grade with a purity higher than or equal to 95% by weight.

The C_2-C_3 olefinic stream, for example ethylene or
propylene, also refinery grade with a purity higher than or

20 equal to 95% by weight, is fed to the alkylation reactor
together with the aromatic hydrocarbon, fresh and, option-
ally, recycled. The two aromatic and olefinic streams are
fed to the alkylation unit so as to have aromatic/olefin
molar ratios which satisfy the requirements of current

25 technologies, generally from 2 to 50, preferably from 3 to

10.

The alkylation reaction is carried out with conventional catalytic systems, for example it can be carried out according to the method described in European patent

5   432,814.

Any alkylation reactor can be used in the process object of the present invention. For example fixed bed or fluid bed reactors, carrier reactors, reactors operating with a slurry mixture and catalytic distillation reactors,

10   can be used.

The preferred alkylation catalysts can be aluminum trichloride or those selected from synthetic and natural porous crystalline solids based on silicon and aluminum, such as acid zeolites in which the silicon/aluminum atomic

15   ratio ranges from 5/1 to 200/1. In particular, Y, beta, omega zeolites, mordenite and the crystalline porous solids MCM-22, MCM-36, MCM-49, are preferred. Alternatively, it is possible to use synthetic zeolites of the ZSM group in which the silicon/aluminum atomic ratio ranges from 20/1 to

20   200/1 such as ZSM-5 zeolite.

The alkylation reaction can be carried out under temperature and pressure conditions which depend not only on the catalyst selected but also on the type of reactor and choice of reagents. In the case of the alkylation of ben-

25   zene with ethylene, the reaction temperature generally

ranges from 50 to 450°C. More specifically, with zeolitic
catalysts, for either fixed or mobile bed processes in gas
phase, the temperature preferably ranges from 300 to 450°C
or from 180 to 250°C for processes in liquid phase, whereas
5   in the case of a catalytic distillation reactor, operating
in mixed gas-liquid phase, the reaction temperature, vary-
ing along the catalytic bed, ranges from 140 to 350°C,
preferably from 200 to 300°C. When reactors operating with
a slurry mixture and an aluminum trichloride catalyst, are
10   used, the temperature ranges from 100 to 200°C.

The pressure inside the alkylation reactor is main-
tained at values ranging from 0.3 to 6 MPa, preferably from
0.4 to 5 MPa.

The aromatic stream leaving the alkylation reactor is
15   treated with conventional means for recovering the reaction
product from the non-converted reagents and reaction by-
products. In particular, the separation system preferably
consists of a series of at least three distillation columns
from which the non-reacted aromatic compound is recovered
20   from the first, and recycled to the alkylation reactor
and/or a transalkylation unit described below. The mono-
alkyl substituted aromatic compound, for example ethyl ben-
zene, is recovered from the second distillation column and
fed to the dehydrogenation unit, whereas the dialkylated
25   aromatic products are recovered from the head of the third

column and sent to the transalkylation unit, whereas the heavy products, essentially consisting of polyalkylated products, tetralines and alkyl substituted diphenyl ethanes, which form the polymerization inhibitor additive, are recovered from the bottom and fed to the purification/separation section of the vinyl aromatic compound.

The dialkylated aromatic compounds, for example diethyl benzenes, can be fed to a transalkylation reactor for transalkylation with C_6-C_9 aromatic hydrocarbons, for example benzene, to produce the corresponding mono-alkyl substituted aromatic compounds, such as ethyl benzene, and increase the yield of the alkylation production.

The transalkylation can take place in a specific reactor or in the same alkylation reactor.

The transalkylation reactor, when present, preferably consists of a reactor operating in slurry phase, when the catalyst is aluminum trichloride, or in a fixed bed reactor, functioning in liquid phase, in which a conventional zeolitic transalkylation catalyst is present, such as Y zeolite, beta zeolite or mordenite, preferably Y or beta zeolite. The transalkylation reaction can be carried out according to what is described in European patent 847,802.

In the case of the transalkylation of diethyl benzene with benzene, the benzene/ethylene molar ratio, calculated with respect to the total moles of benzene present as such

and as diethyl benzene and the total moles of ethylene present as substituents in the diethyl benzenes, ranges from 2/1 to 18/1, preferably from 2.5/1 to 10/1. The temperature in the reactor is maintained at a value of 50 to 350°C,

5 preferably from 130 to 290°C, whereas the pressure is maintained at 0.02 to 6 MPa, preferably from 0.4 to 5 MPa.

The mono-alkylated aromatic product is fed to the catalytic dehydrogenation section which comprises one or more reactors operating with a fixed bed or fluid bed,

10 preferably with a fixed bed.

The dehydrogenation reaction with a fixed bed reactor takes place at a temperature ranging from 500 to 700°C, preferably from 550 to 650°C, at a pressure ranging from 0.02 to 0.15 MPa, in the presence of a catalyst based on

15 iron oxide and potassium carbonate containing other metallic compounds in small quantities having the function of promoters.

In the case of the production process of styrene, the dehydrogenation can take place, for example, with a fixed

20 bed catalyst by feeding a mixture of ethyl benzene vapour and water vapour, in a water/ethyl benzene molar ratio ranging from 5 to 15, preferably from 6 to 12, onto a first reactor in which a partial conversion of ethyl benzene takes place. The reacted mixture leaving the first reactor

25 is fed to a second reactor, after the temperature has been

brought to the required value by means of a heat exchanger. The reaction mixture, in which the ethyl benzene is converted for at least 60%, is cooled and condensed before being sent to the purification section. If required, at the

5   outlet of the second reactor, it is possible to include a third reactor to increase the conversion of ethyl benzene up to and over 70%.

The reaction product leaving the dehydrogenation phase is fed to a second purification/separation section for the

10   recovery of the vinyl aromatic monomer, for example styrene. The purification section comprises at least one distillation column even if it is preferable to operate with three or four distillation columns connected in series with respect to the flow of the monomer to be purified.

15   The heavy bottom product coming from the separation section of the alkylated product is also fed to the second purification/separation section in order to prevent the premature polymerization of the vinyl aromatic monomer and limit the consumption of polymerization inhibitor and/or

20   retardant additives which are necessarily and conventionally used in this section. The feeding can be effected in any of the distillation columns, at any height thereof and, optionally, by premixing said heavy bottom product with any of the streams present in said second purifica-

25   tion/separation section.

In particular, the columns of the second purification/separation section can be selected from those which contain conventional trays or random and/or structured packing. In order to keep the internal temperatures as low as possible to prevent the thermal polymerization of the vinyl aromatic monomer, the columns operate at a low pressure, generally ranging from 0.002 to 0.03 MPa.

In addition to the liquid mixture coming from the dehydrogenation section, a small flow is also fed to the single columns, containing a substance which acts as polymerization inhibitor, for example (in the case of the purification and separation of styrene) 4-hydroxy-2,2,6,6-tetramethyl-piperidin-1-oxy, 2,2,6,6-tetra-methyl-piperidin-1-oxy, or any of the products described in US patent 4,670,131, and in some cases also a further flow which contains a substance which acts as polymerization retardant, for example sulfur, t-butyl catechol or dinitrophenols and phenylene diamines described in US patent 4,466,905. This means of operating limits the loss of vinyl aromatic monomer due to its polymerization which transforms it into a high-boiling product, subsequently eliminated as residue.

The bottom product recovered at the bottom of the third or fourth distillation column consists of a stream rich in high-boiling products, of which a considerable

quantity consists of vinyl aromatic polymer formed in the purification section itself as a result of the distillation process and can still contain a significant quantity of monomer. This stream is a waste product of the process

5   which is generally sent for thermo-destruction.

From what is specified above, it is therefore evident that one of the most important objectives of the purification process of vinyl aromatic monomers is to adopt solutions useful for minimizing the formation of polymer as

10   much as possible, to improve the efficiency of the process by limiting the formation of waste product, and to avoid fouling phenomena associated therewith which can cause operating problems and the necessity for expensive maintenance.

15   The bottom stream leaving the separation section of the alkylated products, consisting of a mixture of polyalkylated aromatic hydrocarbons together with other heavy impurities, is fed to one of the distillation columns, preferably the first column. This stream not only acts as a

20   diluent of the distillation column residues allowing a greater recovery of the monomer but also, surprisingly, as a polymerization retardant, contributing to redce the overall quantity of waste product of the entire process as well as allowing a reduction in the consumption of the sub-

25   stances which inhibit or retard polymerization. As this

stream essentially consists of high-boiling compounds, it
flows through the residues of the distillation column of
the second purification/separation section and is extracted
from the bottom of the last column together with the resi-
5   dues associated with the dehydrogenation. For the above
reasons, the stream deriving from the bottom of said column
in the process scheme object of the present invention, to
be sent for thermo-destruction, is significantly reduced
with respect to the sum of the two corresponding separated
10 streams deriving respectively from the purification section
of the alkyl aromatic product and the vinyl aromatic mono-
mer in the traditional processes of the known art.

   An example is provided below which demonstrates the
inhibiting effect, on the polymerization of styrene, of the
15 bottom product coming from the purification unit of the
synthesis section of ethyl benzene and an applicative exam-
ple which uses a scheme illustrated in the enclosed figure.

EXAMPLE 1

   A first solution of inhibitor 4-HT (1-oxy-2,2,6,6-
20 tetramethyl piperidin-4-ol) in styrene at a concentration
of 5 ppm (test A) and a second solution in styrene of the
same inhibitor at 5 ppm and 1.5% of polyethyl benzenes
(PEB) coming from the bottom of the purification unit of a
plant for the production of ethyl benzene (test B), are
25 prepared in a feeding vessel. In both tests A and B, the

solution containing the inhibitor is fed for about 18 hours in continuous, into a mechanically stirred jacketed reactor and maintained at a temperature of 95°C. The product leaves the reactor by means of a valve situated on the bottom. The

5 feeding and discharge flow-rate are regulated so as to have a constant residence time inside the reactor equal to an hour.

Before each test, the system is treated by nitrogen bubbling in order to eliminate the oxygen and the apparatus

10 is maintained under a nitrogen seal for the whole duration of the test. At the end of 18 hours a sample of effluent corresponding to the stationary state of the system (so-called "zero time") is removed and the polymer content is determined (weight %).

15 This determination is effected by turbidimetry if the concentration of the polymer is lower than 1000 ppm or by precipitation with ethanol for higher quantities.

The feeding is then interrupted and the valve situated on the bottom of the reactor is contemporaneously inter-

20 cepted, thus closing the system on itself (so-called shut off). Samples are taken from the reactor at pre-established times for an overall duration of the test of 7 hours, fol-lowing the formation kinetics of the polymer in the pres-ence of the residual inhibitor at that given temperature.

25 The following table indicates the results of the most

significant tests (polymer content in weight %), effected
at a temperature of 95°C, which unequivocally show the re-
tarding effect of the PEB.

<u>Table 1</u>

Shut off time (min)	Polystyrene % (4-HT) Test A	Polystyrene % (4-HT + PEB) Test B
0	0	0
60	1.7	0.11
120	2.9	0.39
180	4.5	0.60
240	6.5	0.93
360	9.8	1.95
420	11.6	2.36

EXAMPLE 2

        Reference is made to the enclosed figure which repre-
sents a simplified scheme of a process on an industrial
scale for the production and purification of styrene, and
in which the main operating steps are exclusively indi-
cated.

        In the scheme R1 represents the alkylation reactor, R2
is the dehydrogenation reactor, D1 is the first separation
section to recover the alkylated aromatic hydrocarbon
whereas D2 represents the second purification/separation
section of the dehydrogenated product.

The numbered streams and respective weight flow-rates are illustrated and explained in Table 2 below.

R1 = alkylation/transalkylation reactor

Temperature   170°C

5   Pressure   4.6 barA

Benzene/ethylene weight ratio   7.4

R2 = dehydrogenation reactor

Temperature   600°C

Pressure   0.5 barA

10   Table 2

(1) = Fresh benzene	kg/h	19,000
(2) = ethylene	kg/h	5,700
(3) = alkylated product	kg/h	54,700
(6) = recycled benzene	kg/h	23,000
(4) = ethyl benzene for dehydrogenation	kg/h	32,000
(5) = recycled diethyl benzene	kg/h	7,000
(7) = PEB fed to D2	kg/h	300
(12) = PEB fed to the torch	kg/h	300
(8) = Dehydrogenated product	kg/h	32,000
(9) = TEMPO	kg/h	3.6
(10) = Styrene in the case of (7)	kg/h	20,070
(10) = Styrene in the case of (12)	kg/h	20,000
(11) = heavy products in the case of (7)	kg/h	460
(11) = heavy products in the case of (12)	kg/h	230

TEMPO = 1-oxy-2,2,6,6-tetramethyl piperidin-4-ol

25